Frustrated classical Heisenberg model in one dimension with nearest-neighbor biquadratic exchange: Exact solution for the ground-state phase diagram

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The ground-state phase diagram is determined exactly for the frustrated classical Heisenberg chain with added nearest-neighbor biquadratic exchange interactions. There appear ferromagnetic, incommensurate-spiral, "up-up-down-down" (uudd) phases, and disordered states. The model contains an isotropic version of the antiferromagnetic next-nearest-neighbor Ising model, i.e., an *isotropic Ising model*. It is closely related to a model proposed for some manganites, suggesting a possible mechanism for the observed uudd state.

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Frustrated spin systems have been of interest for well over half a century,[1,2] with an increase in activity over the last 10–20 years. One important motivation for recent interest is the role played by complex magnetic order in multiferroics, many examples of which are found in insulating manganites.[3,4] A recent work in Ref. 5 investigated the source of the puzzling "up-up-down-down"(uudd) spin ordering found in several manganites, e.g., $HoMnO_3$. It claimed to find that state in a classical Heisenberg model on a square lattice with ferromagnetic nearest-neighbor interactions and certain competing antiferromagnetic second-nearest-neighbor interactions (which break the square symmetry). However, that conclusion has been shown to be incorrect, this state not occurring in the model.[6] Thus the question as to the source of that state remained unanswered.

Thinking along the lines of generalization of the model of Ref. 5 led to the model discussed in the present Brief Report, as follows. It is well known that the ground state of the famous antiferromagnetic next-nearest-neighbor Ising (ANNNI) model,[7,8] a frustrated Ising model, has the dimension $d=1$ version of the uudd ground state when the ratio NNN to NN interactions is greater than a critical value. But it is also true that anisotropy involving the Mn ions in these materials is small, which seemed to deny relevance of Ising models, which are of course highly anisotropic.

It was realized, however, that biquadratic interactions, $H_{bi}=-\Sigma A_{ij}(\mathbf{S}_i\cdot\mathbf{S}_j)^2$, obviously isotropic, have very Ising-type ground states for $A_{ij}>0$: they all consist of collinear states like Ising states, but unlike the latter they include the states obtained from all rotations of the direction to which the spins are all parallel or antiparallel. In fact it can be seen that for H_{bi} the ground-state entropy per spin in the thermodynamic limit (TL) is ln 2, the same as for the (noninteracting) Ising model. In addition, as discussed below, such terms can be large. Thus it became clear that study of a model incorporating frustrated Heisenberg interactions plus biquadratic terms was important to the search for the origin of the uudd state. In addition to the introduction of an "isotropic Ising model," the model studied here incorporates, as special cases, models studied in a considerable body of literature. Other efforts aimed at the uudd question,[9,10] based on very different scenarios, will be discussed below. The present work is also related to the phenomenological mimicking, via H_{bi}, the order-selecting effects of thermal, quantum, or dilution fluctuations,[11] so-called "order by disorder,"[12] as will be seen.

To get a feeling for the qualitative behavior of the type of model relevant to the manganite question, we consider the $d=1$ example

$$H=\sum [J_1\mathbf{S}_n\cdot\mathbf{S}_{n+1}+J_2\mathbf{S}_n\cdot\mathbf{S}_{n+2}-A(\mathbf{S}_n\cdot\mathbf{S}_{n+1})^2],\quad \mathbf{S}_l^2=1. \tag{1}$$

This, with $J_1<0, J_2>0$, is the model that will be addressed; the ground state depends only on $\gamma=J_2/|J_1|$ and $a=A/|J_1|$.[13] The model with $a=0$ is the well known simplest model exhibiting spiral ground states (see, e.g., Refs. 14 and 15), and the replacement $\mathbf{S}_n\cdot\mathbf{S}_m\rightarrow S_n^z S_m^z$ gives the ANNNI model for the ground state. The case $\gamma=J_2/|J_1|=0$ has been widely studied.[16–22] The J_2 term will be seen to introduce very different physics. Because of an essentially one-dimensional quality of the model considered vis á vis the manganite problem,[5,6] the qualitative behavior for that model with added NN biquadratic interactions is expected to be similar.

Biquadratic exchange is known to be experimentally important. For example, one of the earliest works indicating appreciable effect of such interactions is in the paramagnetic resonance experiments of Harris and Owen,[23] that studied the NN-pair spectrum of Mn^{2+} ions in MgO. They find that $j=0.05J$ in the Hamiltonian $J\mathbf{S}_a\cdot\mathbf{S}_b-j(\mathbf{S}_a\cdot\mathbf{S}_b)^2$ gives a rather good fit to their measurements. The assumption that the coefficient 0.05 indicates a small effect would be wrong: The correction to the Heisenberg term is almost 100% for some of the Landé intervals. This comes from the large spin factors involved. Perhaps the earliest paper on the model of Heisenberg+biquadratic interactions on a lattice is that of Rodbell *et al.*[24] for rock-salt structure antiferromagnets, MnO and NiO. They assumed $a>0$, and found large stiffening of the sublattice magnetization relative to the Heisenberg theory for the usual collinear spin states,[25] and good agreement with experiment. In these cases H_{bi} removes a degeneracy involving noncollinearity of antiferromagnetic sublattices, providing an example related to the work of Henley.[11,26] However the qualitative behavior is not similar to that found in the present work. The microscopic origin and an order-of-magnitude estimate of H_{bi} were discussed by Anderson.[27] For more recent work see Ref. 28, and references therein, and below.

A recent example of the phenomenological use of H_{bi} to simulate the "order-by-disorder" effect is in Ref. 29, where a three-dimensional model of competing Heisenberg interactions plus biquadratic terms and anisotropies and external magnetic field; this model was "solved" by trying many different stationary states. In the present simpler case, the ground state is found rigorously.

The well-known Luttinger-Tisza method (see the review in Ref. 1) appears to be not useful for finding the ground state of Eq. (1), because of the nonlinearity introduced into the equations for stationarity of H subject to the weak constraint, $\Sigma_j(J_{ij}-2A_{ij}\mathbf{S}_i\cdot\mathbf{S}_j)\mathbf{S}_j=\lambda\mathbf{S}_i$. Instead I turn to the rather unknown cluster method of Lyons and Kaplan (LK),[14] which is tractable and solves the problem exactly. Briefly recall that method. Assuming periodic boundary conditions with the TL to be taken finally.[14] Then one easily verifies that Eq. (1) can be rewritten as

$$H=\sum_i H_c(\mathbf{S}_{i-1},\mathbf{S}_i,\mathbf{S}_{i+1}), \tag{2}$$

where the "cluster energy"

$$H_c(\mathbf{S}_1,\mathbf{S}_2,\mathbf{S}_3)=\frac{1}{2}\{J_1(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3)-A[(\mathbf{S}_1\cdot\mathbf{S}_2)^2+(\mathbf{S}_2\cdot\mathbf{S}_3)^2]\}+J_2\mathbf{S}_1\cdot\mathbf{S}_3 \tag{3}$$

involves three neighboring spins. Clearly

$$H\geq\sum_i \min H_c(\mathbf{S}_{i-1},\mathbf{S}_i,\mathbf{S}_{i+1}). \tag{4}$$

One can easily find the minimum of H_c. If the corresponding state "propagates," i.e., if there is a state of the system such that every set of three successive spins gives the minimum H_c, then according to Eq. (4), this state will be a ground state of H. This is the LK cluster method as applied to this case. The method is not limited to one dimension or to translationally invariant Hamiltonians.[14]

To minimize H_c, first consider coplanar states, and label the angles θ,θ' made by the end spins with the central spin, assumed with no loss of generality to be up. The cluster energy is, with $h_c=H_c/|J_1|$,

$$h_c(\theta,\theta')=-\frac{1}{2}(\cos\theta+\cos\theta')+\gamma\cos(\theta-\theta')-\frac{a}{2}(\cos^2\theta+\cos^2\theta'), \tag{5}$$

where $a=A/|J_1|$. Solutions of $\frac{\partial h_c}{\partial\theta}=\frac{\partial h_c}{\partial\theta'}=0$ are

$$(\theta,\theta')=(0,0),(0,\pi),(\pi,0),(\pi,\pi)(\text{Ising type})$$

and

$$(\theta,\theta')=(\theta_0,-\theta_0),(\text{spiral type}),$$

where

$$\cos\theta_0=-\frac{1}{2(2\gamma-a)}\quad\text{for}\quad|2(2\gamma-a)|\geq 1. \tag{6}$$

The (π,π) solution (which leads to the ordinary antiferromagnetic state) is never lowest because we have assumed

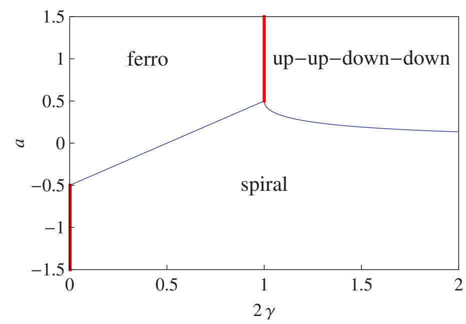

FIG. 1. (Color online) Phase diagram: $a\equiv A/|J_1|$ vs $2\gamma\equiv 2J_2/|J_1|$. Disorder occurs on the emphasized vertical line segments.

$J_1<0$. The (0,0) solution obviously propagates as the ferromagnetic state. The solutions $(\pi,0),(0,\pi)$, i.e., $(\downarrow,\uparrow,\uparrow),(\uparrow,\uparrow,\downarrow)$ plus their degenerate reversed spin counterparts can easily be seen to propagate in the up-up-down-down state.[14] The solution $(\theta_0,-\theta_0)$, degenerate with its uniform rotations, obviously propagates in a simple spiral $\mathbf{S}_n=\hat{x}\cos n\theta_0+\hat{y}\sin n\theta_0$, $\hat{x},\hat{y}$ being any pair of orthonormal vectors. Such states were first discussed long ago;[15,30,31] more generally, for arbitrary Bravais lattices with general J_{ij}, it was shown[32] that the corresponding spiral, $\hat{x}\cos\mathbf{q}\cdot\mathbf{n}+\hat{y}\sin\mathbf{q}\cdot\mathbf{n}$, minimizes the classical Heisenberg energy for the appropriate wave vector $\mathbf{q}$. See Ref. 1 for a recent review. In the present case, the cluster method provides a proof (alternate to the Luttinger-Tisza method used in Refs. 1 and 32) for the purely Heisenberg case. Because of the isotropy of the biquadratic terms, the cluster method accomplishes the proof just as easily.

I list the energies for the various stationary solutions

$$h_{ferro}=h_c(0,0)=-1-a+\gamma$$

$$h_{uudd}=h_c(0,\pi)=-a-\gamma$$

$$h_{spiral}=h_c(\theta_0,-\theta_0)=-\gamma-\frac{1}{4(2\gamma-a)}. \tag{7}$$

The spiral energy holds only for the condition in Eq. (6). Equating these energies in pairs yields the boundaries of the regions shown in Fig. 1. As a check, to make sure no stationary states of h_c were missed, I calculated the energy difference across boundaries over a mesh of values of θ and θ' varying independently over $-\pi$ to π. For example, I calculated $h_c(\theta,\theta')-h_{uudd}$ at $(2\gamma,a)=(1.5,0.1)$ and (1.5,0.25), the former being in the spiral region, the latter in the uudd region. The former showed some negative values, the latter only positive values, as required.

The possibility of noncoplanar states was examined by allowing an azimuthal angle for one of the cluster spins; no noncoplanar stationary states were found to exist.

Figure 2 shows the variation in q with γ for $a=0.2$. In the ferromagnetic and spiral regions, $q=\theta_0$, the spiral wave vector; in the uudd region, $2\pi/q$ is the repeat distance of the

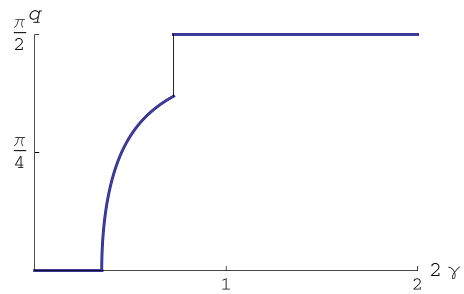

FIG. 2. (Color online) q vs 2γ at $a=0.2$; period or wavelength $\equiv 2\pi/q$.

spin state. q is continuous across the spiralferro boundary, discontinuous across the spiral-uudd boundary, as seen in the example of Fig. 2.

In Fig. 1, at $a=0$ it is seen that the ferro→spiral transition occurs at the well-known value $\gamma=1/4$.[14,15,25] For large a the uudd state is seen, as expected from the qualitative argument given earlier; at $a \geq 0.5$ the transition ferro→uudd occurs at the same value, $\gamma=1/2$ as in the ANNNI model,[7,14] hence the name isotropic Ising model for this region. At $\gamma=0$, the transition ferro→spiral occurs at $a=-1/2$, in agreement with the finding of Thorpe and Blume (TB)[17] (their J_2 is my $-a$); in that work only $a<0, \gamma=0$ is considered. Furthermore, they find that the state on the line $a<-1/2$ is disordered; this is not inconsistent with the present finding, which implies only a spiral in the limit $\gamma \to 0$; *at* $\gamma=0$ the state is indeed highly degenerate, since it depends only on the angle between nearest neighbors, so that for a given spin $\mathbf{S}_n, \mathbf{S}_{n+1}$ can lie anywhere on a cone with $\mathbf{S}_n$ as axis and 1/2-angle θ_0, giving a (one-dimensionally) macroscopic entropy. Introduction of the second neighbor Heisenberg interaction removes this degeneracy.

The ferromagnetic transition at $a=-1/2$ on the line $\gamma=0$ shows the following interesting effect. Starting from $a=0$, adding the extra interaction (the biquadratic terms) of sufficient strength causes the transition ferromagnet→TB disordered state. This is like the inverse of the order-by-disorder effect.[11,12,26] In the present case, adding the biquadratic terms increases the entropy as a passes through—0.5. That is, the introduction of an additional interaction (usually thought to lower degeneracy, in the spirit of the Nernst "theorem"), causes the opposite effect, an *increase* in entropy: "disorder-by-order." The same effect occurs as a increases past $+1/2$ at $\gamma=1/2$: this line segment, $a \geq 1/2$ is an extension of the "multiphase point" of the ANNNI model,[7] at which the spins are disordered. This effect is the opposite of the ordering tendency of H_{bi} discussed in Refs. 11 and 29.

A surprise is that the spiral state continues for negative γ. The straight-line ferrospiral boundary, $a=2\gamma-1/2$, continues to $-\infty$ as $\gamma \to -\infty$. q or θ_0 vs γ at fixed $a<-1/2$ changes continuously to zero as the ferrospiral boundary is approached from the right. Nothing special happens at $\gamma=0$, despite the macroscopic degeneracy at (and only at) that point. The spiral in this region is caused by the competition between the all-ferromagnetic Heisenberg exchange and the biquadratic exchange (the latter "likes" noncollinear spins with angle between NN spins of $\pi/2$). The NNN interaction γ removes the macroscopic degeneracy (as for the antiferromagnetic case).

The finding of the uudd ground state is of course relevant to the paper of Kimura *et al.*,[5] and its refutation,[6] presented above as a motivation for the present study. It reopens the possibility of a frustrated exchange model being behind the uudd state, involving not only competition between Heisenberg exchange terms but also between them and biquadratic exchange.

In this connection, I note a very different path to the uudd state, namely, the model where the NN exchange varies from ferromagnetic to antiferromagnetic, in continuing periodic fashion. This, with no other interactions, trivially leads to the uudd state in the one-dimensional model (the magnetic interactions are noncompeting). This model is very close to the mechanism proposed by Zhou and Goodenough[9] for the same manganites discussed in Ref. 5. The alternating sign of the NN exchange interaction in the a-b plane of these materials is argued, quite reasonably, as being caused by the complex structure of the Jahn-Teller distortion.[9] The effect of appreciable further-neighbor interactions, widely believed to be behind the spiral structures that occur in many other insulating manganites,[3,4] needs consideration.

The other work[10] that addresses the uudd state in the same manganites, and the origin of the spirals found in other manganites, is based on a 2-e_g-band model with infinite Hund's rule coupling J_h between e_g and t_{2g} electrons (and between the latter as well). Intra-atomic Coulomb interactions, U, generally larger than J_h, and (unlike the 1-band model) relevant to the 2-band model, are neglected.[33] The work claims to find the uudd state.

In summary, the ground state of the classical frustrated Heisenberg model plus biquadratic exchange interactions has been solved analytically in one dimension through an exact cluster method.[14] The phase diagram shows ferromagnetic, spiral, up-up-down-down, and disordered spin states. The uudd state is an example of an isotropic Ising model, and the biquadratic exchange terms are essential to its realization. Given the refutation[6] of the competing Heisenberg exchange model of Ref. 5, the present work reopens the possibility of a competing exchange interaction model being behind the observed uudd state, unifying the theory with that underlying many other manganites, as an alternative to the magnetically nonfrustrated model of Zhou and Goodenough.[9] Which of these very different scenarios actually applies to the observations awaits further study, both theoretical and experimental.

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